ABSTRACT OF FINAL REPORT

PRF # 1836 - A1

TITLE OF GRANT Complexes of β-Dicarbonyl Dianions

PRINCIPAL INVESTIGATOR J. A. Bertrand

INSTITUTION Georgia Institute of Technology

Bis(2,4-pentanedionato)metal(II) compounds react with base in methanol to form compounds of the general formula

$$[M(Acac)(OCH_3)(CH_3OH)_x]_y$$

where Acac represents the anion of 2,4-pentanedione.

For the magnesium, cobalt, and nickel compounds (1,2), analyses and molecular weight data indicate that x = 1 and y = 4. The structure of the cobalt(II) compound (3) has been determined by a single crystal X-ray diffraction study. The four cobalt(II) ions of one molecule form a tetrahedron; a methoxide ion is located over each face of the tetrahedron with the methoxide oxygen approximately equidistant from the three cobalt(II) ions defining the face. The two oxygens of a pentanedionato- group and the oxygen of a methanol molecule complete the slightly distorted octahedral coordination of the cobalt(II) ion; spectral and magnetic properties of this compound and the corresponding nickel compound also indicate octahedral coordination. Diffraction photographs of the nickel and magnesium compounds indicate similar structures.

For the copper(II) compound (4), x = 0 and y = 2; the magnetic moment of 0.8 B. M. is indicative of super-exchange and infrared, ultraviolet, and visible spectra are consistent with square planar coordination with bridging

methoxide groups.

Complexes of the same general type have been prepared with other alkyl groups in place of the methyl groups of the methoxide and/or the methanol; complexes with other β-dicarbonyl anions have also been prepared (1).

Attempts to prepare similar copper(II) complexes with hexafluoroacetylacetone were unsuccessful, but the studies (5) led to the isolation of anhydrous bis(hexafluoroacetylacetonato)copper(II) as well as the dihydrate (which had previously been reported as the anhydrous compound); a dimeric monomethanolate was also isolated.

REFERENCES

(1) J. A. Bertrand and D. Caine, J. Am. Chem. Soc., 86, 2298 (1964).

(2) R. I. Kaplan, M. S. Thesis, Georgia Institute of Technology, 1966.

(3) J. A. Bertrand and R. I. Kaplan, 154th Meeting, American Chemical Society, Chicago, Ill., September, 1967.

(4) J. A. Bertrand and R. I. Kaplan, Inorg. Chem., 4, 1657 (1965).

(5) J. A. Bertrand and R. I. Kaplan, Inorg. Chem., 5, 489 (1966).

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Bis(2,4-pentanedionato)metal(II) compounds react with base in methanol to form compounds of the general formula

$$[M(Acac)(OCH_3)(CH_3OH)_x]_y$$

where Acac represents the anion of 2,4-pentanedione.

For the magnesium, cobalt, and nickel compounds (1,2), analyses and molecular weight data indicate that x = 1 and y = 4. The structure of the cobalt(II) compound (3) has been determined by a single crystal X-ray diffraction study. The compound crystallizes as monoclinic crystals (a= 21.79 Å, b= 10.91 Å, c= 20.21 Å, β= 121.7°) of space group C 2/c with four tetramers per unit cell. A total of 1557 reflections have been refined to an R value (conventional) of 0.10.

As expected from molecular weight data, the compound is tetrameric. The four cobalt(II) ions of one molecule form a tetrahedron; a methoxide ion is located over each face of the tetrahedron with the methoxide oxygen approximately equidistant from the three cobalt(II) ions defining the face (the six crystallographically different Co - OCH_3 bonds vary from 2.04 Å to 2.14 Å). The two oxygens of a pentanedionato group and the oxygen of a methanol complete the slightly distorted octahedral coordination of the cobalt(II) ion (bond angles at cobalt vary from 81° to 100°; Co - O bond lengths vary from 2.01 Å for one of the 2,4-pentanedionato oxygens to

2.20 Å for the methanol oxygen).

Spectral and magnetic properties of this compound and the corresponding nickel compound also indicate octahedral coordination; diffraction photographs of the nickel and magnesium compounds indicate similar structures.

By heating these compounds in vacuum at 100° C., the methanol can be removed; molecular weight studies and infrared spectra indicate that the same type of structure is present after removal of the methanol and the metal ions are, thus, five-coordinate.

For the copper(II) compound (4), x = 0 and y = 2; the magnetic moment of 0.8 B. M. is indicative of super-exchange and infrared, ultraviolet, and visible spectra are consistent with square planar coordination with bridging methoxide groups.

Complexes of the same general type have been prepared with other alkyl groups in place of the methyl groups of the methoxide and/ or the methanol; complexes with other β-dicarbonyl anions, such as those of salicylaldehyde and o-hydroxyacetophenone, have also been prepared (1).

Attempts to prepare similar copper(II) complexes with hexafluoroacetylacetone were unsuccessful, but the studies (5) led to the isolation of anhydrous bis(hexafluoroacetylacetonato)copper(II) as well as the dihydrate (which had previously been reported as the anhydrous compound); a dimeric monomethanolate was also isolated.

Reactions of the methoxide compounds with alcohols have been investigated. Boiling the copper(II) compound in alcohols results in replacement of the methoxide groups by the alkoxide of the higher boiling alkoxide when primary alcohols are used and results in the formation of bis(2,4-pentanedionato)copper(II) and copper alkoxides when other alcohols are employed;

the Cu(Acac)(OR) compounds formed are dimeric and have low magnetic moments similar to that of the methoxide compound.

Reaction of the nickel(II) compound with secondary alcohols resulted in replacement of the methanol by the secondary alcohol but no replacement of the methoxide occurred; reaction with primary alcohols appeared to result in replacement of methoxide as well as methanol but satisfactory analyses of these products have not been obtained.

Attempts have been made to prepare a cobalt(III) complex by reaction of the cobalt(II) compound with hydrogen peroxide in methanol but, due to the insolubility and/or stability of the cobalt(II) compound, no oxidation resulted; attempts to react bis(2,4-pentanedionato)cobalt(II) with potassium hydroxide in methanol and in the presence of hydrogen peroxide resulted in the formation of a hydroxide complex, $[Co(Acac)(OH)(CH_3OH)]_4$, when the reaction was carried out at room temperature and resulted in the formation of the methoxide complex when the reaction mixture was refluxed.

Complexes of trivalent transition metal ions containing a chelated 2,4-pentanedionato group and methoxide groups have been prepared by reacting tris(2,4-pentanedionato)iron(III) and tris(2,4-pentanedionato)cobalt(III) with potassium hydroxide in methanol.

Acknowledgment is made to the donors of The Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

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(1) J. A. Bertrand and D. Caine, J. Am. Chem. Soc., 86, 2298 (1964).

(2) R. I. Kaplan, M. S. Thesis, Georgia Institute of Technology, 1966.

(3) J. A. Bertrand and R. I. Kaplan, 154th Meeting, American Chemical Society, Chicago, Ill., September, 1967.

(4) J. A. Bertrand and R. I. Kaplan, Inorg. Chem., 4, 1657 (1965).

(5) J. A. Bertrand and R. I. Kaplan, Inorg. Chem., 5, 489 (1966).

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CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY,
GEORGIA INSTITUTE OF TECHNOLOGY,
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Preparation and Properties of Di-μ-methoxo-bis(2,4-pentanedionato)dicopper(II)

BY J. A. BERTRAND AND ROY I. KAPLAN

Received June 1, 1965

Several complexes containing both methoxide and β-dicarbonylate ions have been reported[1,2]; these can be represented by the general formula $MA(OCH_3)(CH_3OH)_x$. A beryllium complex,[1] with A representing the anion of 3-nitro-2,4-pentanedione and $x = 0$, was reported to have a molecular weight corresponding to a mixture of dimeric and trimeric species; cobalt(II) complexes,[2] with A representing the anion of salicylaldehyde, *o*-hydroxyacetophenone, or 2,4-pentanedione and $x = 1$, were found to have much higher associations. Complexes of nickel(II) and magnesium(II),[2] prepared by the same method used for cobalt(II), were analogous to the cobalt(II) complexes; however, copper(II) complexes prepared by the same method did not separate from solution as large crystals as did the other complexes, the solids did not lose weight on heating, and analyses indicated a formula similar to the beryllium complex. We have investigated the copper(II) complex of 2,4-pentanedione further and report here the results of those investigations.

(1) R. M. Klein and J. C. Bailar, Jr., *Inorg. Chem.*, **2**, 1189 (1963).
(2) J. A. Bertrand and D. Caine, *J. Am. Chem. Soc.*, **86**, 2298 (1964).

Experimental

Preparation of Di-μ-methoxo-bis(2,4-pentanedionato)dicopper(II).—A 1.8-g. (0.007 mole) sample of bis(2,4-pentanedionato)copper(II) was dissolved in 350 ml. of refluxing methanol and 0.39 g. (0.007 mole) of potassium hydroxide was added dropwise to the refluxing solution. The solution was refluxed for 2 hr. and filtered while hot. The compound was obtained as a violet, microcrystalline solid.

Anal. Calcd. for $C_6H_{10}O_3Cu$: C, 37.2; H, 5.6. Found: C, 37.1; H, 5.3.

The compound is soluble in acetonitrile, chloroform, dichloromethane, nitromethane, and pyridine.

Spectral Measurements.—Spectra in the visible and ultraviolet were obtained with a Carey Model 14 spectrophotometer. Chloroform was used as solvent.

The infrared spectrum was obtained with a Perkin-Elmer

Model 21 spectrophotometer. Both a Nujol mull and a chloroform solution were run.

Molecular Weight Determination.—The molecular weight was obtained with a Mechrolab vapor pressure osmometer at 37° using chloroform as solvent. Values of 439, 403, and 395 were obtained for 0.0125, 0.0250, and 0.0500 *F* solutions, respectively.

Magnetic Susceptibility Determination.—The magnetic susceptibility of the compound was measured at room temperature with a Gouy balance. The uncorrected molar susceptibility was 215×10^{-6} c.g.s. unit and was independent of field strength.

Results and Discussion

The copper(II) complex differs from the other divalent transition metal complexes both in formulation and in association. Although the other complexes were highly associated, the degree of association varying with concentration, the copper(II) compound was essentially dimeric in chloroform at all concentrations.

The magnetic moment of the compound was calculated using the expression $\mu_{eff} = 2.84[\chi_m^{cor} - N\alpha)T]^{1/2}$. A diamagnetic correction of -78×10^{-6} was used and a value of $N\alpha$ of 60×10^{-6} per copper ion was assumed. The value obtained, 0.75 B.M., was considerably below the value for one unpaired electron.

The dimeric nature, the low magnetic moment, and the tendency of copper(II) to achieve four-coordination suggest that there are bridging groups present in the compound. Although there is no bridging by the oxygens of bis(2,4-pentanedionato)copper(II),[3] such bridging is known to exist in trimeric bis(2,4-pentanedionato)nickel(II)[4] and in tetrameric bis(2,4-pentanedionato)cobalt(II)[5] and it is possible that the 2,4-pentanedione oxygens are the bridging groups in this compound. The methoxide ion often acts as a bridging

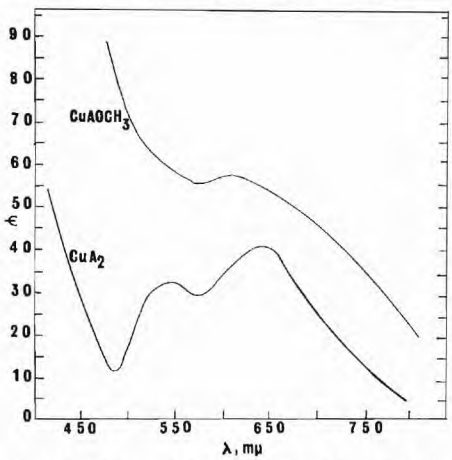


Figure 1.—Visible spectra of di-μ-methoxo-bis(2,4-pentanedionato)dicopper(II) and bis(2,4-pentanedionato)copper(II). Extinction coefficients are based on formula weight per copper(II) ion.

group,[6] and it seems more probable that the methoxides are the bridging groups; however, there is some evidence of both bridging and terminal methoxides in copper(II) methoxide.[7]

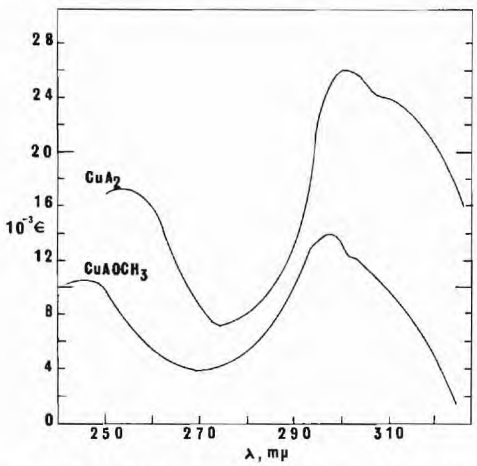


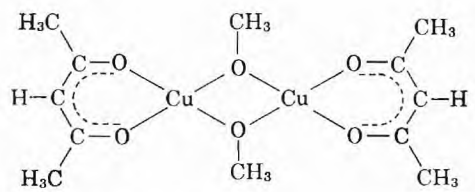
Figure 2.—Ultraviolet spectra of di-μ-methoxo-bis(2,4-pentanedionato)dicopper(II) and bis(2,4-pentanedionato)copper(II). Extinction coefficients are based on formula weight per copper(II) ion.

It has been suggested[6] that bridging methoxides have a carbon–oxygen stretching below 1040 cm.$^{-1}$, while terminal methoxides absorb above 1060 cm.$^{-1}$. Since only one band, at 1018 cm.$^{-1}$, is observed in this region for the copper(II) complex, it appears that only bridging methoxides are present in this compound.

Assuming that the dimer is bridged by the methoxides, there is still the possibility of at least two different structures for the complex; either a planar or a tetrahedral arrangement could exist. A series of complexes with bridging oxygens, $[Cu(pyO)Cl_2]_2$ (where pyO represents various substituted pyridine N-oxides), has been reported,[8] and all of the compounds have low magnetic moments; the structure of the compound containing unsubstituted pyridine N-oxide has been determined[9] and shows a distorted tetrahedral arrangement around the copper. However, a large number of copper(II) compounds, including bis(2,4-pentanedionato)copper(II),[3] are square-planar.

The visible spectrum of this complex, Figure 1, consists of a broad band centered around 16,000 cm.$^{-1}$. The absorption is similar in wave length and in intensity to that of bis(2,4-pentanedionato)copper(II) and other square-planar complexes of copper(II); tetrahedral complexes of copper(II) with oxygen donors do not absorb in the visible region, the weaker crystal field causing a shift to lower energy.[10]

Although other structures may be possible, the experimental evidence is consistent with a planar, dimeric structure



(3) H. Koyama, Y. Saito, and H. Kuroya, *J. Inst. Polytech., Osaka City Univ.*, **C4**, 43 (1953).

(4) G. J. Bullen, R. Mason, and P. Pauling, *Inorg. Chem.*, **4**, 456 (1965).

(5) F. A. Cotton and R. C. Elder, *J. Am. Chem. Soc.*, **86**, 2294 (1964).

(6) C. G. Barraclough, D. C. Bradley, J. Lewis, and I. M. Thomas, *J. Chem. Soc.*, 2601 (1961).

(7) C. H. Brubaker, Jr., and M. Wicholas, *J. Inorg. Nucl. Chem.*, **27**, 59 (1965).

(8) W. E. Hatfield, Y. Muto, H. B. Jonassen, and J. S. Paschal, *Inorg. Chem.*, **4**, 97 (1965).

(9) H. L. Schafer, J. C. Morrow, and H. M. Smith, *J. Chem. Phys.*, **42**, 504 (1965).

(10) C. J. Ballhausen, "Introduction to Ligand Field Theory," McGraw-Hill Book Co., New York, N. Y., 1962, p. 272.

It is possible to rule out, in addition to tetrahedral structures and structures containing bridging carbonyl oxygens, any structure which would significantly alter the chelate ring since the ultraviolet spectrum of this compound and that of bis(2,4-pentanedionato)copper(II), Figure 2, are identical except for intensity (the bands of the methoxide complex are approximately half as intense); the infrared absorptions of the 2,4-pentanedionato group are similar in the two compounds.

An X-ray investigation to confirm the suggested structure had been planned, but numerous attempts to obtain single crystals of the compound have failed.

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Contribution from the School of Chemistry,
Georgia Institute of Technology, Atlanta, Georgia

A Study of Bis(hexafluoroacetylacetonato)copper(II)[1]

By J. A. Bertrand and Roy I. Kaplan

Received October 12, 1965

Although bis(hexafluoroacetylacetonato)copper(II) has been the subject of several studies,[2-4] there appears to be some confusion about the characterization

(1) Supported by the Petroleum Research Fund of the American Chemical Society under Grant No. 1836-A1. Presented at the Southeast–Southwest Regional American Chemical Society Meeting, Memphis, Tenn., Dec. 1965.

(2) R. L. Belford, A. E. Martell, and M. Calvin, *J. Inorg. Nucl. Chem.*, **2**, 11 (1956).

(3) J. P. Fackler, Jr., F. A. Cotton, and D. W. Barnum, *Inorg. Chem.*, **2**, 97 (1963).

of this substance. In the first published report[2] of this compound, the carbon and hydrogen analyses of the green, sublimed product checked for a dihydrate; however, no absorptions characteristic of water were present in the infrared spectrum and the substance was, thus, characterized as the anhydrous compound; in a later study,[3] analytical data for copper checked very well with the value expected for the anhydrous chelate.

In both studies,[2,3] the visible spectrum reported for this compound was considerably different from the spectra of chelates of copper(II) with other substituted acetylacetonates—not only in the position of absorption, which would be indicative of a different ligand field, different π bonding, etc., but a pronounced shoulder on the high-energy side of the visible band of all of the other chelates was not observed in the spectrum of the hexafluoroacetylacetonate.

A more recent study[4] of the infrared spectra of metal hexafluoroacetylacetonates reports absorption characteristic of water for the copper compound and characterizes the compound as a monohydrate; no analytical data were given.

In the course of preparing several copper chelates for further studies, we prepared the hexafluoroacetylacetone compound. Instead of purifying the initial product by sublimation, we first recrystallized it from methanol and then sublimed; the sublimed material was a mixture of green and blue crystals. Since previous studies indicate only a green sublimate, we have carried out further studies on the system.

Experimental Section

Preparation of Bis(hexafluoroacetylacetonato)diaquocopper(II).—Copper nitrate trihydrate (0.09 mole) was dissolved in water (200 ml); to this was added, with mixing, hexafluoroacetylacetone (0.18 mole) and sodium acetate (0.18 mole) in water (20 ml). The green needles which precipitated were filtered and dried in air; the product was further purified by sublimation; mp 134–136°.

Anal. Calcd for $CuC_{10}H_6F_{12}O_6$: C, 23.4; H, 1.17; Cu, 12.4. Found: C, 23.7; H, 1.01; Cu, 12.5.

Preparation of Bis(hexafluoroacetylacetonato)copper(II).—A portion of the dihydrate was placed in a vacuum desiccator over sulfuric acid; the color gradually changed from green to purple. The purple solid melted at 95–98°.

Anal. Calcd for $CuC_{10}H_2F_{12}O_4$: C, 25.1; H, 0.42; Cu, 13.4. Found: C, 23.7; H, 0.60; Cu, 13.4.

A sample of 1.081 g of the purple solid was exposed to the atmosphere until repeated weighings showed no further change in weight. The final weight, 1.158 g, indicated 6.64% water (calculated for the dihydrate, 7.01%).

Anal. Found (after hydration): C, 23.7; H, 1.09; Cu, 12.5.

Physical Measurements.—Infrared spectra were obtained using a Perkin-Elmer Model 21 spectrophotometer. The spectra of the two compounds were identical with the reported spectrum of bis(hexafluoroacetylacetonato)copper(II) except for a band at 3430 cm^{-1} in the dihydrate spectrum.

Visible and near-infrared spectra were obtained using a Cary Model 14 spectrophotometer. Spectra of the two compounds in chloroform were identical with the spectrum previously reported. The spectra of the two compounds in carbon tetrachloride are shown in Figure 1.

Room temperature magnetic moments were obtained using a Gouy balance; values of 1.9 BM were obtained for both compounds.

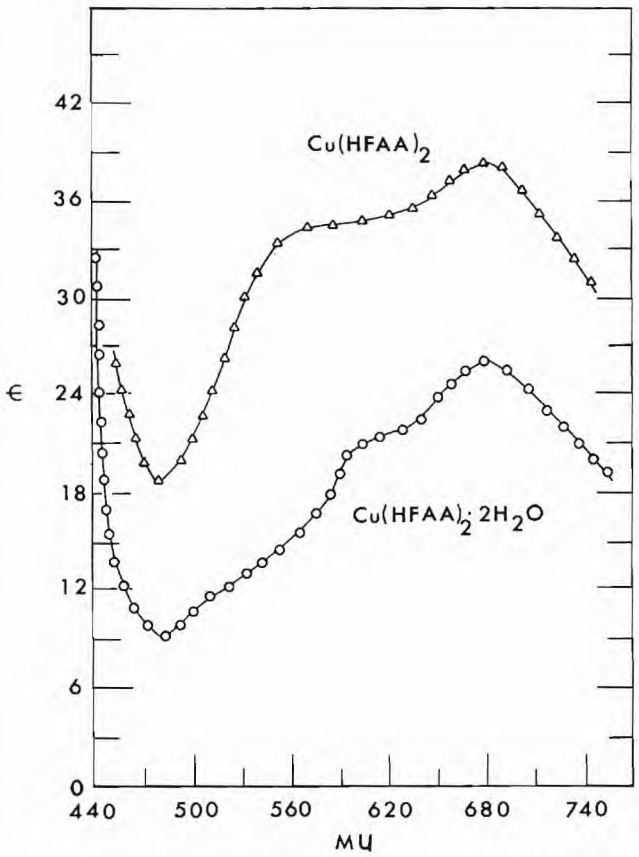

Figure 1.—Visible spectra of carbon tetrachloride solutions of bis(hexafluoroacetylacetonato)copper(II) and its dihydrate.

Molecular weights were obtained using a Mechrolab Model 301A vapor pressure osmometer; carbon tetrachloride was used as solvent. No concentration dependence was noted for any of the compounds; average values of 473 and 496 were obtained for the anhydrous material and the dihydrate, respectively.

Results and Discussion

The previously reported green solid[2,3] appears to be bis(hexafluoroacetylacetonato)diaquocopper(II); although the dihydrate sublimed unchanged, it is dehydrated over sulfuric acid under vacuum to the purple anhydrous material. These conclusions are supported by the analytical data and by infrared spectra of the two compounds which show absorptions characteristic of water in the spectrum of the green compound but not in the spectrum of the purple compound.

The stability of the dihydrate is surprising when compared to the tendency of other β-dicarbonyl chelates of copper(II) to form adducts. Although such adducts have been noted in solution[5] and a few have been isolated as solids,[6] the stability of square-planar copper(II) complexes causes a marked decrease in the tendency to form octahedral adducts as are common, for example, with cobalt(II) and nickel(II) β-dicarbonyl compounds. It has been noted[4] that the hexafluoroacetylacetonates of these metals form very stable hydrates whereas the acetylacetonates form hydrates which are readily dehydrated.

Both the anhydrous compound and the dihydrate

(5) D. P. Graddon, *Nature*, **183**, 1610 (1959).

(6) R. D. Gillard and G. Wilkinson, *J. Chem. Soc.*, 5399 (1963), and references cited therein.

were found to be monomeric and both exhibited normal magnetic moments. The visible spectrum of the anhydrous material in carbon tetrachloride, Figure 1, shows a well-separated shoulder on the high-energy side of the visible band; the spectrum of the dihydrate in the same solvent shows a less pronounced shoulder much closer to the main band. Since a well-separated shoulder is present on the high-energy side of the main band in the spectra of all other β-dicarbonyl complexes of copper(II), this shoulder probably results from further splitting of the d orbitals as the symmetry is decreased from octahedral to square-planar; such an assignment has been discussed for bis(acetylacetonato)-copper(II).[7] The position of this band, nearer the main band, in the dihydrate spectrum is probably due to a less pronounced tetragonal distortion and, thus, suggests that the waters are coordinated to the copper to give a distorted octahedron.

(7) T. S. Piper and R. L. Belford, *Mol. Phys.*, **5**, 169 (1962).

D. ANNUAL PERSONNEL STATEMENT

(1 copy due October 1)

PRF # 1836 - A1

RESEARCH TITLE: Complexes of β-Dicarbonyl Dianions

INSTITUTION: Georgia Institute of Technology

PRINCIPAL INVESTIGATOR: J. A. Bertrand

UNDERGRADUATE SCHOLARS, PREDOCTORAL FELLOWS
OR ASSISTANTS, AND POSTDOCTORAL FELLOWS
SUPPORTED UNDER ABOVE NAMED ACS-PRF GRANT

NAME	AGE	1/ UNDERGRADUATE SCHOOL	COUNTRY OF PERMANENT RESIDENCE	2/ DEGREE(S) GRANTED	DATES SUPPORT WAS REC'D
None - small amount remaining was used only for supplies					

1/ For graduate students, indicate the name of College or University attended prior to graduate work.

2/ List the degree or degrees obtained as a result of research conducted under PRF sponsorship.

E. LIST OF PUBLICATIONS ACKNOWLEDGING PRF SUPPORT

PRF # 1836 - A1

Investigator: J. A. Bertrand

In order to have a complete and accurate record of publications acknowledging PRF support we ask each principal investigator to enter the titles and literature references for such publications below. This list will become a part of the record of each grant and will be returned annually to the principal investigator for revision. Please use the format illustrated by the following example.

(1) C. Pierce and B. Ewing, *Physical Adsorption in the Multilayer Region on Heterogeneous and Homogeneous Surfaces*, J. Am. Chem. Soc. 84, 4070 (1962).

(1) J. A. Bertrand and R. I. Kaplan, "Preparation and Properties of Di-μ-methoxo-bis(2,4-pentanedionato)dicopper(II)," Inorg. Chem., 4, 1657 (1965).

(2) J. A. Bertrand and R. I. Kaplan, "A Study of Bis(hexafluoroacetylacetonato)-copper(II)," Inorg. Chem., 5, 489 (1966).